Supplemental Information for

Mechanical improvement of calcium carbonate cements by *in situ* HEMA polymerization during hardening

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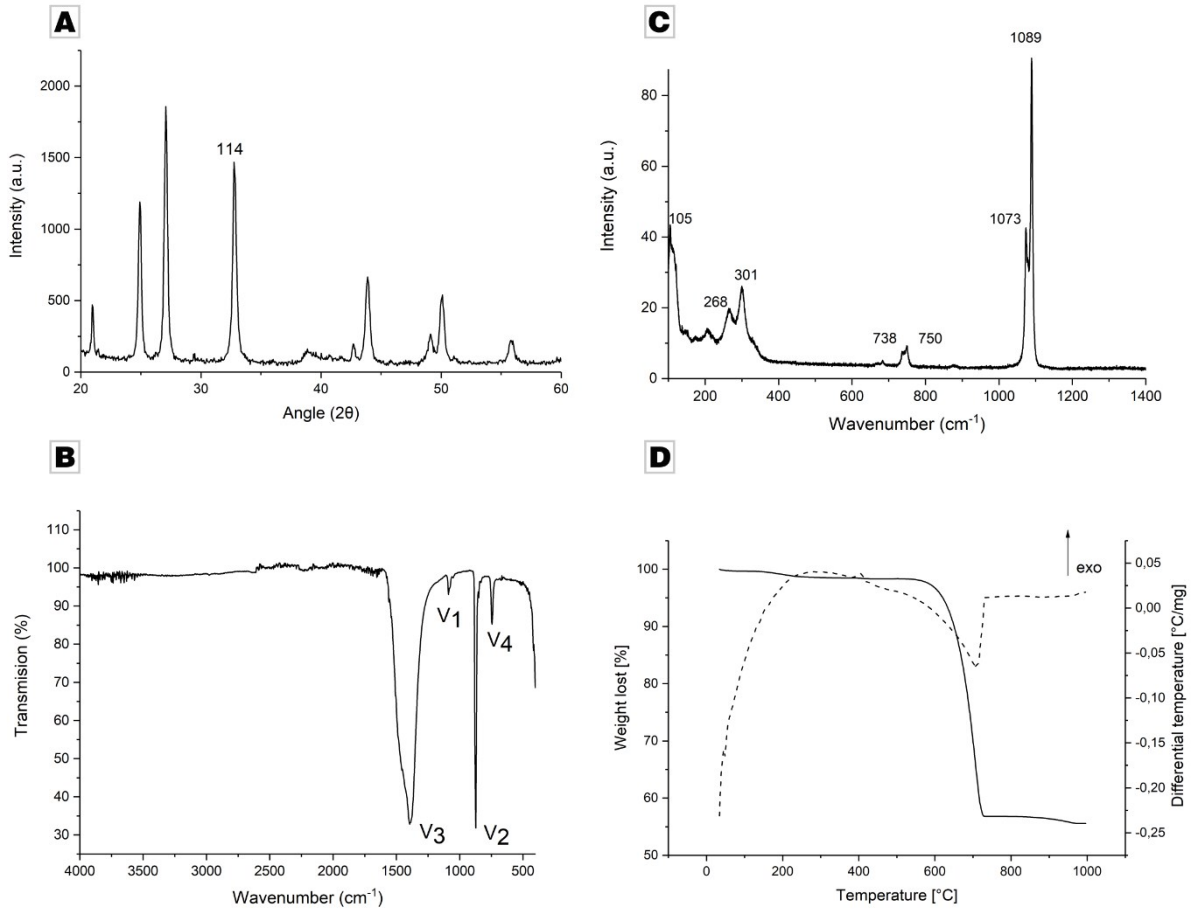

Figure S1. Characterization of synthetic vaterite. The phase purity was assured by XRD (**A**) and was further corroborated by ATR/FTIR analysis (**B**). The corresponding ATR/FTIR spectrum shows the characteristic absorption bands of vaterite while bands characteristic for aragonite or calcite were absent.[1,2] Raman spectroscopy confirmed this (C). The precipitated vaterite powder was also characterized by TG-DTA (D) which revealed the presence of 0.5 wt.% of physisorbed water and 1.0–1.5 wt.% water incorporated as crystal water.[3] The major weight loss in the temperature range of 500–800 °C (~42.0 wt.%), accompanied by an endothermic peak at 715 °C in the DTA curve, which caused by the expected thermal decomposition of $CaCO_3$ to CaO and CO_2. The TG-DTA analysis documents also the absence of an amorphous phase.

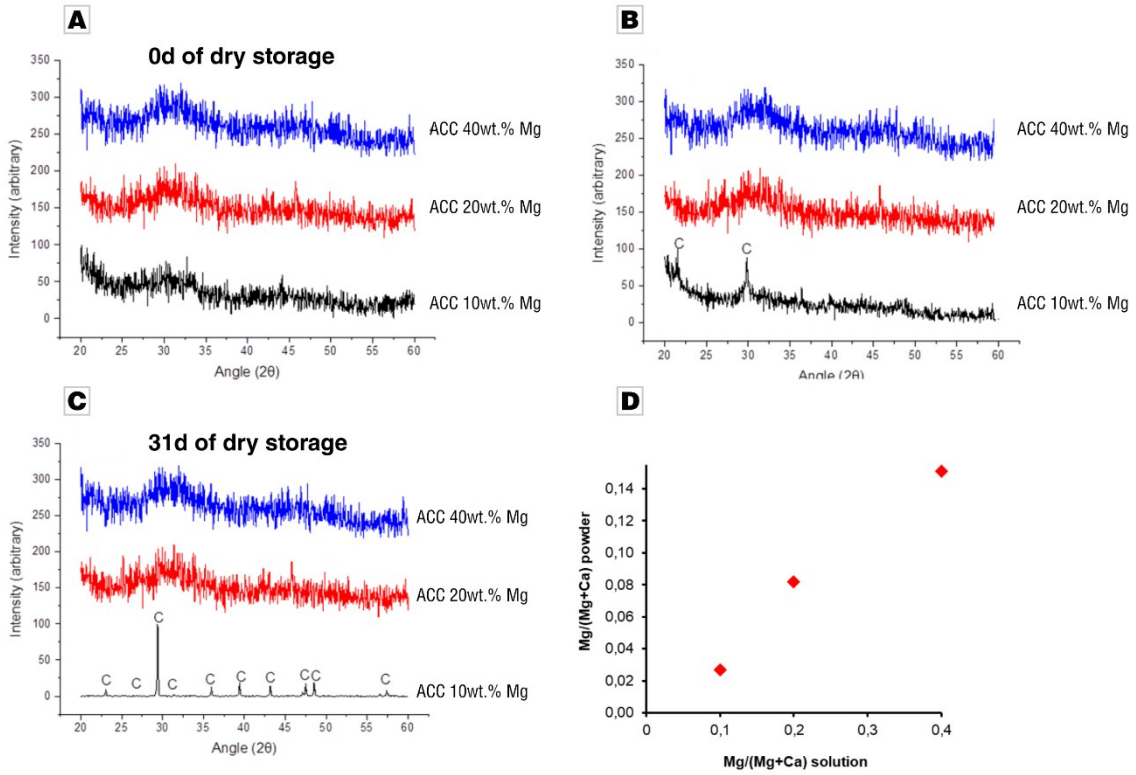

Figure S2. Characterization of synthetic ACC. (**A)** XRD patterns of ACC powders freshly synthesized with 10, 20, 40 wt.% magnesium after synthesis. (**B)** Mg-ACC samples after 7 days of storage in dry state, (**C)** after 31 days in dry state. (**D)** Weight ratio Mg/(Mg + Ca) in the precipitated ACC powders as determined by ICP-MS, plotted against the ratio Mg/(Mg + Ca) in the starting solution.

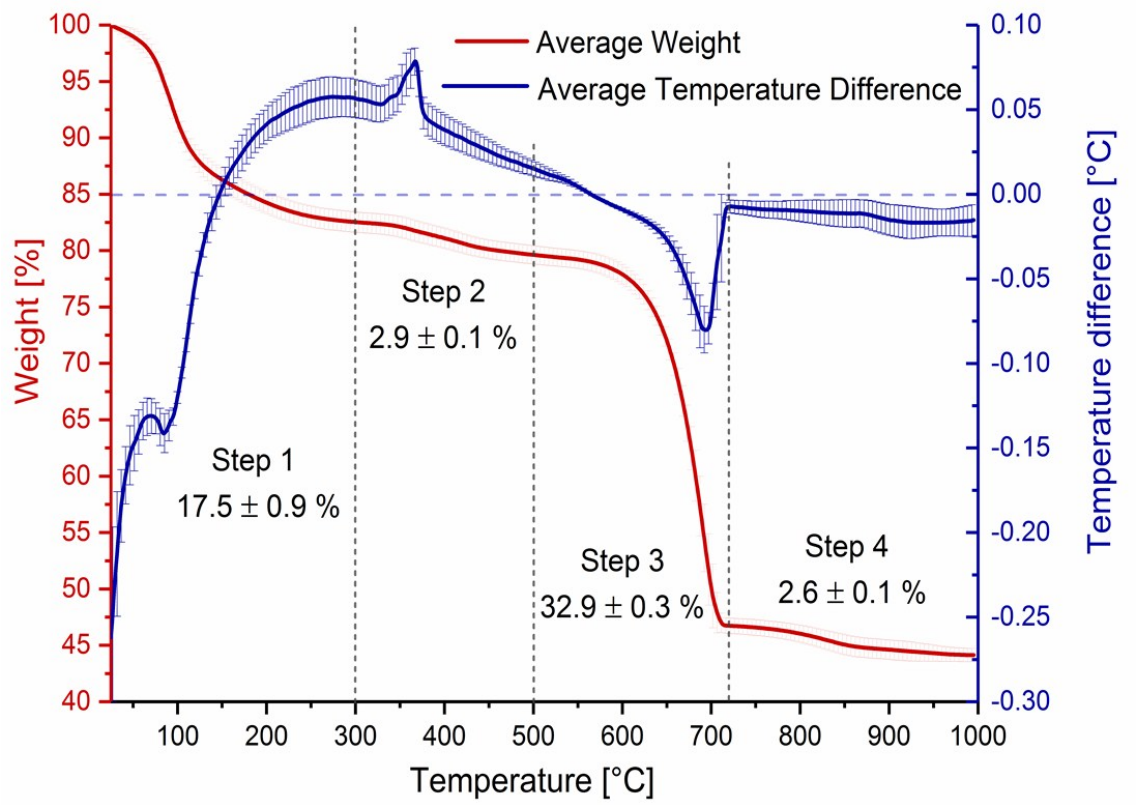

Figure S3. DTA-TGA results of ACC_20Mg, performed with a heating rate of 5 °C / min; the mean values of three independent measurements are presented, the error bars give the standard deviation. The decomposition shows four major steps, and an incipient weight loss can already be spotted at the very beginning of the TGA measurement. Below 150 °C, weight loss is caused by the loss of non-bound water incorporated in the ACC matrix. At 150 °C, the DTA signal indicated an exothermic reaction which was accompanied by a slight weight loss. In step 2, only a slight weight loss was recorded while a remarkable exothermic DTA signal occurred at 364 ± 3 °C. Since this event was not accompanied by a correspondingly sharp weight loss, this indicates a phase transformation of ACC to a crystalline phase, probably calcite. In step 3, the rapid weight loss was accompanied by a clear endothermic DTA signal; we assign this to the thermal decomposition of the Mg-doped $CaCO_3$.

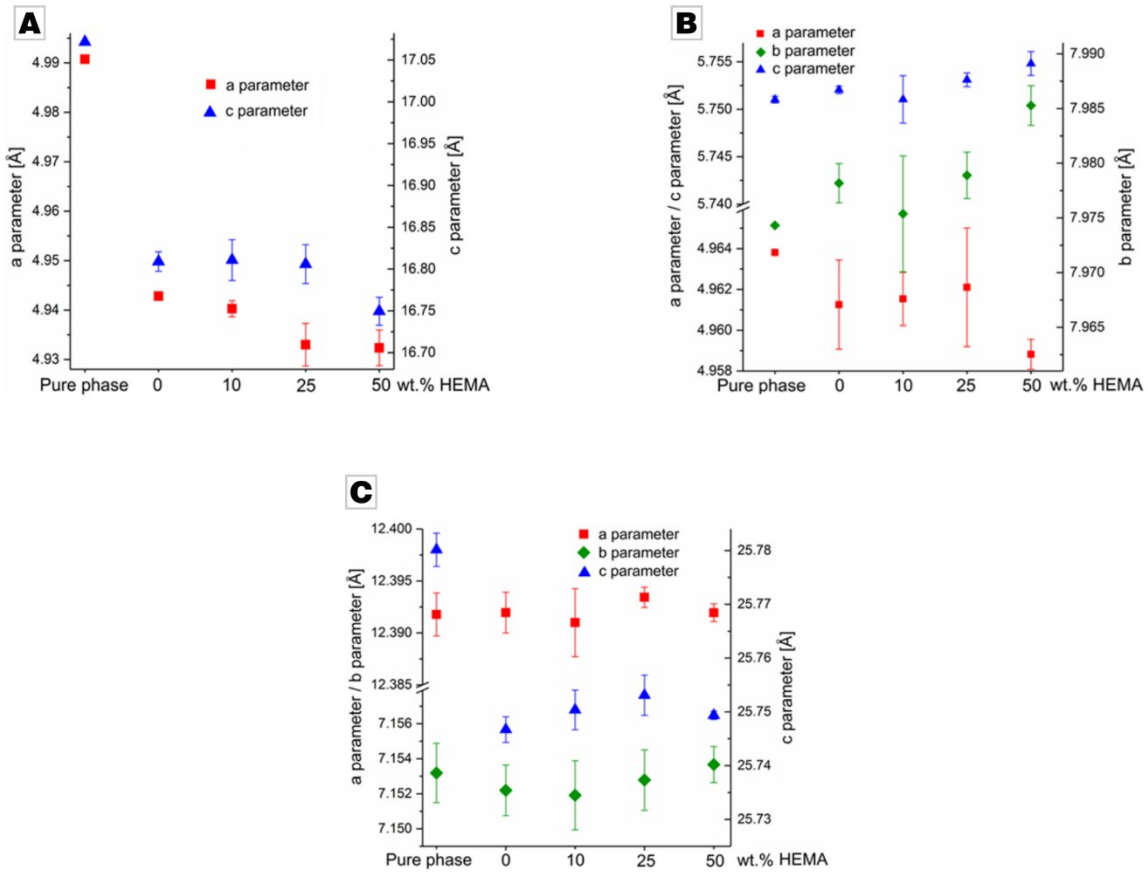

Figure S4. Lattice parameters of (**A)** calcite, (**B)** aragonite, and (**C)** vaterite, as determined by Rietveld refinements; the mean values of three independently prepared measurements are shown.

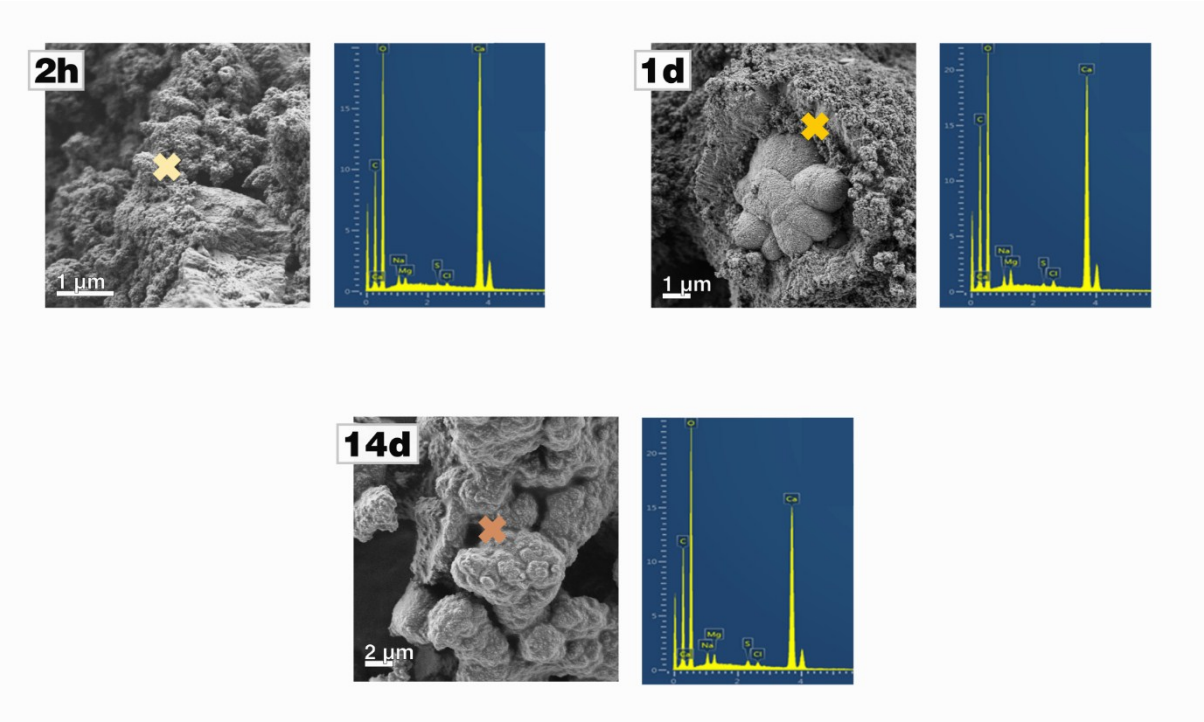

Figure S5. EDS measurements of fractured surfaces of crushed cements after different times of settlement. The initial formulation of the cement before setting was ACC_Mg20 : V = 1:2, LPR = 1 mL/g, 50 wt.% HEMA.

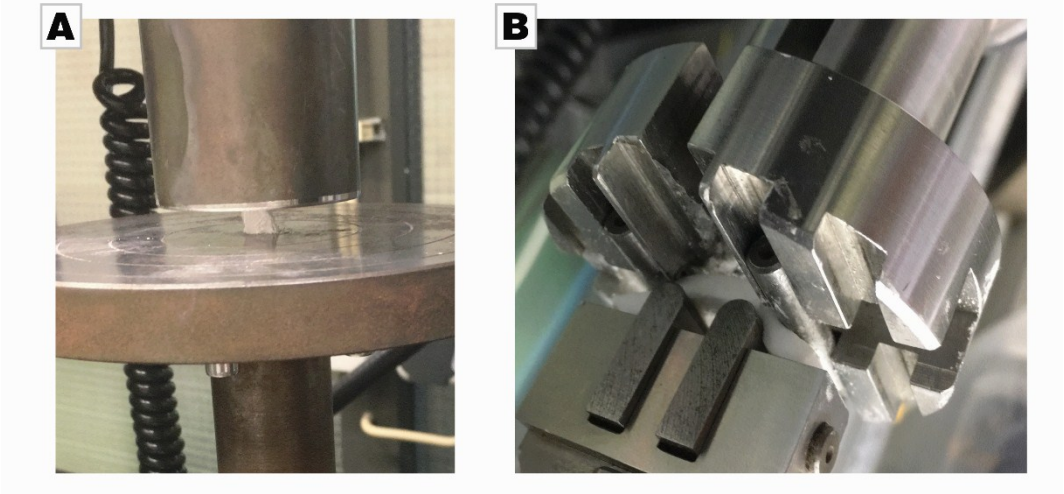

Figure S6. Optical images of **(A)** compression and **(B)** four-point bending tests on a cement with 50wt% HEMA. The initial formulation of the cement before setting was ACC_Mg20 : V = 1:2, LPR = 1 mL/g, 50 wt.% HEMA.

References

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